6L

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION**	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
P22296PC00		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/NL 99/ 00568	13/09/1999	11/09/1998
Applicant		
COÖPERATIEVE VERKOOP- EN PRODUCTIEVEREN...et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 03 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readble form.

   [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. ---

   [ ] as suggested by the applicant.

   [ ] because the applicant failed to suggest a figure.

   [ ] because this figure better characterizes the invention.

   [ ] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 99/00568

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08B31/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 975 206 A (LOTZGESELL ET AL.) 17 August 1976 (1976-08-17) column 3, line 9 - line 29 claims; table 1	1-9
A	US 3 539 366 A (FOSTER G. EWING) 10 November 1970 (1970-11-10) column 2, line 40 - line 46 claims	1-3,5,6, 8,9

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 December 1999	09/12/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Mazet, J-F

1

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	P. PAROVUORI ET AL.: "Oxidation of potato starch by hydrogen peroxide" STÄRKE, vol. 47, no. 1, 1995, pages 19-23, XP002091292 de page 19, left-hand column, line 29 - line 36 page 20, line 11 - line 32 page 21, right-hand column, line 9 - line 19 ---	1-6,8
A	R. L. WHISTLER ET AL.: "Oxidation of amylopectin with hydrogen peroxide at different hydrogen ion concentrations" THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 81, 1959, pages 3136-3139, XP002091293 usa page 3138, left-hand column, line 47 -right-hand column, line 27 ---	1
A	CHEMICAL ABSTRACTS, vol. 123, no. 12, 18 September 1995 (1995-09-18) Columbus, Ohio, US; abstract no. 147114, "Substitued succinic anhydride-containing sizing emulsions for surface sizing of newsprint paper" XP002091294 abstract & JP 07 138898 A (ARAKAWA CHEM IND) 30 May 1995 (1995-05-30) ---	10
A	US 3 655 644 A (H. W. DURAND) 11 April 1972 (1972-04-11) cited in the application -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/NL 99/00568

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3975206 A	17-08-1976	NONE	
US 3539366 A	10-11-1970	NONE	
JP 07138898 A	30-05-1995	NONE	
US 3655644 A	11-04-1972	NONE	

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Assistant Commissioner for Patents
United States Patent and Trademark Office
Box PCT
Washington, D.C.20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing: 23 March 2000 (23.03.00)	
International application No.: PCT/NL99/00568	Applicant's or agent's file reference: P22296PC00
International filing date: 13 September 1999 (13.09.99)	Priority date: 11 September 1998 (11.09.98)
Applicant: KESSELMANS, Ronald, Peter, Wilhelmus et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International preliminary Examining Authority on:

11 January 2000 (11.01.00)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer:

J. Zahra

Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92bis.1 and Administrative Instructions, Section 422)

To:

OTTEVANGERS, S., U.
Vereenigde
Nieuwe Parklaan 97
NL-2587 BN The Hague
PAYS-BAS

Date of mailing (day/month/year)
14 April 2000 (14.04.00)

Applicant's or agent's file reference
P22296PC00

IMPORTANT NOTIFICATION

International application No.
PCT/NL99/00568

International filing date (day/month/year)
13 September 1999 (13.09.99)

1. The following indications appeared on record concerning:

[ ] the applicant [ ] the inventor [X] the agent [ ] the common representative

Name and Address
OTTEVANGERS, S., U.
Vereenigde Octrooibureaux
Nieuwe Parklaan 97
NL-2587 BN The Hague
Netherlands

State of Nationality:
State of Residence:
Telephone No.: 070-4166711
Facsimile No.: 070-4166799
Teleprinter No.:

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

[ ] the person [ ] the name [X] the address [ ] the nationality [ ] the residence

Name and Address
OTTEVANGERS, S., U.
Vereenigde
Nieuwe Parklaan 97
NL-2587 BN The Hague
Netherlands

State of Nationality:
State of Residence:
Telephone No.: 070-4166711
Facsimile No.: 070-4166799
Teleprinter No.:

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

[X] the receiving Office
[ ] the International Searching Authority
[X] the International Preliminary Examining Authority
[ ] the designated Offices concerned
[X] the elected Offices concerned
[ ] other:

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Facsimile No.: (41-22) 740.14.35

Authorized officer
G. Bähr
Telephone No.: (41-22) 338.83.38

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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
P22296PC00		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/NL99/00568	13/09/1999	11/09/1998

International Patent Classification (IPC) or national classification and IPC
C08B31/18

Applicant
COÖPERATIEVE VERKOOP- EN PRODUCTIEVEREN...et al.

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
11/01/2000	07.07.2000

Name and mailing address of the international preliminary examining authority:

European Patent Office
D-80298 Munich
Tel. +49 89 2399 - 0 Tx: 523656 epmu d
Fax: +49 89 2399 - 4465

Authorized officer

Gerber, M

Telephone No. +49 89 2399 8528

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL99/00568

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-16 as originally filed

Claims, No.:

1-10 as originally filed

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-10
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-10
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-10
	No:	Claims	

2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Novelty

Claims 1-10 are novel over the available prior art since none of the documents of the international search report discloses an oxidation process carried out on waxy tuber starch with hydrogen peroxide.

2. Inventive step

The process claimed in claims 1-7, as well as the oxidised starch claimed in claim 8 and the use thereof claimed in claims 9 and 10 are considered to be inventive.

D2, which represents the most relevant state of the art, discloses an oxidising process of potato and tapioca starches, various modified starches and derivatives of starch such as esters and ethers. Said process comprises employing hydrogen peroxide (0,035-0,7 wt.% based on dry starch) in combination with a catalyst, as for example copper sulfate (0,008-0,03 wt.%, based on starch dry substance), in aqueous suspension. Calcium carbonate can be added to the reaction medium in order to keep the pH in a certain range. A process according to D2 is supposed to lead to a starch solution of predictable viscosity and showing a good temperature stability.

The subject-matter of claim 1 differs from D2 in the amylopectin-content of the starch to be oxidised and the use of significantly smaller amounts of a divalent copper catalyst.

The problem to be solved by the present invention may therefore be regarded as to select a type of root or tuber starch suitable for being oxidised using hydrogen peroxide and a divalent copper catalyst in small amount, to get an oxidised starch having a low viscosity and high viscosity stability upon storage when in solution.

The solution proposed in claim 1 of the present application is considered as involving an inventive step (Article 33(3) PCT) for the following reasons.

None of the documents suggests the use of waxy tuber starch or the reduction of the amount of divalent copper ions necessary as a catalyst to achieve a reasonable degree of oxidation within a reasonably short time.

The amounts of copper ions used in D2 are far larger than the amounts used in the present application. The disclosure of D2 does not teach anything about the reduction of copper concentration.

As can be seen from example 1, table 1, the hydrogen peroxide degradation of starch catalysed by small amounts of copper ions is the most efficient for amylopectin potato starch. The addition of copper ions is necessary to increase the reaction rate (represented by the negative result of the peroxide test). Moreover, 932 ppb of copper-ions are sufficient for the complete conversion of hydrogen peroxide when oxidising amylopectin potato starch, as for regular potato starch this amount reaches 1858 ppb. This leads however to starch solutions with very high viscosity and gelling upon storage, which is not the case of the amylopectin potato starch solutions (see also examples 4 and 5).

Hence, inventive step is present in the subject-matter of claims 1-10.

3. Industrial applicability

The subject-matter of present claims 1-10, relating to the use of oxidised starch in the paper industry, the adhesive industry, the textile industry and the food industry, appears to comply with the requirements of industrial applicability as stipulated in Article 33(4) PCT.

Re Item VIII
Certain observations on the international application

a) The vague and imprecise statement in the description on page 10, lines 8-15, implies that the subject-matter for which protection is sought may be different to that defined by the claims, thereby resulting in lack of clarity (Article 6 PCT) when used to interpret them (see also the PCT Guidelines, III-4.3a).

b) The intrinsic viscosity unit "dL/g" employed on page 2, line 27, on page 10, line 28, page 12, table 1, and on page 13, table 2, is not generally used, contrary to the requirements of Rule 10.1(d) PCT.

c) The term "Merckoquant" on page 10, line 35, appears to be a registered trade mark.

d) The technical term "MSin" employed on page 14, in example 4, is not generally accepted in the art, contrary to the requirements of Rule 10.1(e) PCT.

e) The use of the word "about" in connection with the limits of ranges renders the scope of protection sought by claim 3 unclear.

f) The use of the expression "and the like" on page 8, lines 27 and 28, to extend a list of concrete examples in some ill-defined manner leads to obscurity.

PATENT COOPERATION TREATY

Sup rupp

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

To:

OTTEVANGERS, S.U.,
VEREENIGDE OCTROOIBUREAUX
~~Nieuwe Parklaan 97~~
~~NL-2587 BN The Hague~~
PAYS-BAS

NRF2 11-03-2001

Kopie In/naar | TERMIJN
1 2 JULI 2000

Beantwoord voor/ def. | bericht gezonden aan/ dd

Applicant's or agent's file reference
MAP P22296PC00

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing *(day/month/year)* 07.07.2000

IMPORTANT NOTIFICATION

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/NL99/00568	13/09/1999	11/09/1998

Applicant
COÖPERATIEVE VERKOOP- EN PRODUCTIEVEREN...et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/
European Patent Office
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Tel. +49 89 2399 - 0 Tx: 523656 epmu d
Fax: +49 89 2399 - 4465

Authorized officer
Hardy Magliano, N
Tel.+49 89 2399-8151

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C08B 31/18 — A1

(11) International Publication Number: WO 00/15670

(43) International Publication Date: 23 March 2000 (23.03.00)

(21) International Application Number: PCT/NL99/00568

(22) International Filing Date: 13 September 1999 (13.09.99)

(30) Priority Data:
98203043.9 11 September 1998 (11.09.98) EP

(71) Applicant *(for all designated States except US)*: COÖPERATIEVE VERKOOP- EN PRODUCTIEVERENIGING VAN AARDAPPELMEEL EN DERIVATEN AVEBE B.A. [NL/NL]; Beneden Oosterdiep 27, NL-9641 JA Veendam (NL).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: KESSELMANS, Ronald, Peter, Wilhelmus [NL/NL]; Kromkampen 11, NL-9468 HK Annen (NL). BLEEKER, Ido, Pieter [NL/NL]; Poldermolen 22, NL-9791 LS Ten Boer (NL).

(74) Agent: OTTEVANGERS, S., U.; Vereenigde Octrooibureaux, Nieuwe Parklaan 97, NL-2587 BN The Hague (NL).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: OXIDATION OF STARCH

(57) Abstract

The invention relates to a process of oxidizing starch wherein a root or tuber starch, comprising at least 95 wt.% based on dry substance of the starch of amylopectin, or a derivative thereof, is treated with hydrogen peroxide in the presence of a catalyst, which catalyst comprises divalent copper ions.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

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EE	Estonia	LR	Liberia	SG	Singapore		

Title: Oxidation of starch

The invention relates to the oxidation of starch.

The oxidation of starch is usually carried out in order to reduce the viscosity of the starch in solution or dispersion. During the oxidation reaction, starch molecules are broken down, yielding molecules having a decreased molecular weight.

Oxidized starches have found many applications in industry. Examples of common applications include the use of oxidized starch in the paper industry, for instance in coatings or surface sizing, the adhesive industry, the textile industry, and the food industry.

The preparation of oxidized starches is conventionally carried out by oxidation with an alkali metal hypochlorite, which is a relatively cheap oxidizing agent. The oxidation of starch using an alkali metal hypochlorite is extensively described in the literature (see among others "Modified Starches: Properties and Uses", O.B. Wurzburg, CRC Press Inc., 1987).

Although the oxidation of starch using an alkali metal hypochlorite is an efficient reaction, leading to high yields of desired product in a relatively short reaction time, it has some disadvantages. One disadvantage is that a large amount of salts is produced, in particular chloride salts, during the oxidation. Other disadvantages are the risk of chlorine formation during the reaction and of the occurrence of unacceptably high AOX levels.

In order to overcome the problems associated with these disadvantages, attempts have been made to find an alternative oxidizing agent. One alternative oxidizing agent that has received a significant amount of attention is hydrogen peroxide.

As early as in 1933, in the German Patent 738909, a process has been described wherein starch is oxidized using only hydrogen peroxide as oxidizing agent. The reaction is performed under semi-dry conditions at a temperature below

60°C. The obtained oxidized starch product was intended to be used in puddings. It has meanwhile been found, however, that this process does not lead to a considerable extent of break down of the starch molecules in a reasonable reaction time. In other words, the disclosed process is very slow.

In order to improve the reaction rate of the oxidation of starch using hydrogen peroxide, it has been proposed to use metal catalysts in said oxidation reactions. In the international patent application WO-A-97/35888, it has been proposed to use metal based coordination complexes as catalysts in an alkaline slurry reaction of starch with hydrogen peroxide. The disclosed coordination complexes are based on a transition metal selected from groups VIb, VIIb,, VIIIb or the lanthanide series of the Periodic Table. The complexes further comprise an organic ligand containing at least three nitrogen atoms which coordinate to the metal, and a bridging group.

From US patent 3,655,644, the use of copper as a catalyst in the oxidation of starch using hydrogen peroxide is known. Although the patent mentions general amounts of copper of from 5 to 100 ppm, according to the examples at least 50 ppm needs to be used.

Disadvantages of the known processes for oxidizing starch using hydrogen peroxide and a metal based catalyst are that undesirably high amounts of catalyst (50 ppm) are required in order to be able to degrade the starch to a sufficient extent (intrinsic viscosity 0,1 - 1,5 dL/g) within a reasonable reaction time (less than 24 hours).

The present invention aims to provide a process for oxidizing starch using hydrogen peroxide, which process does not have the disadvantages of the prior art. More in particular, it is an object of the invention to provide a process for oxidizing starch using hydrogen peroxide, which process leads to a sufficiently degraded starch product in a relatively short reaction time.

Surprisingly, it has been found that the above objectives may be reached by starting from a specific type of starch, which has a very low amylose content. Thus, the invention relates to a process of oxidizing starch, wherein a root or tuber starch comprising at least 95 wt.% based on dry substance of the starch of amylopectin, or a derivative thereof, is treated with hydrogen peroxide in the presence of a catalyst, which catalyst comprises divalent copper ions.

In a process according to the invention, very small amounts of the catalyst suffice in order to provide a process having a high reaction rate. The process of the invention leads, in a short time, to an oxidized starch having a desirably low viscosity and high stability, when in solution.

As has been indicated above, according to the invention, a root or tuber starch is oxidized, which starch has a very high amylopectin content. Most starch types consist of granules in which two types of glucose polymers are present. These are amylose (15-35 wt.% on dry substance) and amylopectin (65-85 wt.% on dry substance). Amylose consists of unbranched or slightly branched molecules having an average degree of polymerization of 1000 to 5000, depending on the starch type. Amylopectin consists of very large, highly branched molecules having an average degree of polymerization of 1,000,000 or more. The commercially most important starch types (maize starch, potato starch, wheat starch and tapioca starch) contain 15 to 30 wt.% amylose.

Of some cereal types, such as barley, maize, millet, wheat, milo, rice and sorghum, there are varieties of which the starch granules nearly completely consist of amylopectin. Calculated as weight percent on dry substance, these starch granules contain more than 95%, and usually more than 98% amylopectin. The amylose content of these cereal starch granules is thus less than 5%, and usually less than 2%. The above cereal varieties are also referred to as waxy cereal grains, and the amylopectin starch granules isolated therefrom as waxy cereal starches.

In contrast to the situation of different cereals, root and tuber varieties of which the starch granules nearly exclusively consist of amylopectin are not known in nature. For instance, potato starch granules isolated from potato tubers usually contain about 20% amylose and 80% amylopectin (wt.% on dry substance). During the past 10 years, however, successful efforts have been made to cultivate by genetic modification potato plants which, in the potato tubers, form starch granules consisting for more than 95 wt.% (on dry substance) of amylopectin. It has even been found feasible to produce potato tubers comprising substantially only amylopectin.

In the formation of starch granules, different enzymes are catalytically active. Of these enzymes, the granule-bound starch synthase (GBSS) is involved in the formation of amylose. The presence of the GBSS enzyme depends on the activity of genes encoding for said GBSS enzyme. Elimination or inhibition of the expression of these specific genes results in the production of the GBSS enzyme being prevented or limited. The elimination of these genes can be realized by genetic modification of potato plant material or by recessive mutation. An example thereof is the amylose-free mutant of the potato (amf) of which the starch substantially only contains amylopectin through a recessive mutation in the GBSS gene. This mutation technique is described in, inter alia, J.H.M. Hovenkamp-Hermelink et al., "Isolation of amylose-free starch mutant of the potato (*Solanum tuberosum L.*)", Theor. Appl. Gent., (1987), 75:217-221, and E. Jacobsen et al., "Introduction of an amylose-free (amf) mutant into breeding of cultivated potato, *Solanum tuberosum L.*, Euphytica, (1991), 53:247-253.

Elimination or inhibition of the expression of the GBSS gene in the potato is also possible by using so-called antisense inhibition. This genetic modification of the potato is described in R.G.F. Visser et al., "Inhibition of the expression of the gene for granule-bound starch synthase in

potato by antisense constructs", Mol. Gen. Genet., (1991), 225:289-296.

By using genetic modification, it has been found possible to cultivate and breed roots and tubers, for instance potato, yam, or cassave (Patent South Africa 97/4383), of which the starch granules contain little or no amylose. As referred to herein, amylopectin potato starch is the potato starch granules isolated from potato tubers and having an amylopectin content of at least 95 wt.% based on dry substance.

Regarding production possibilities and properties, there are significant differences between amylopectin potato starch on the one hand, and the waxy cereal starches on the other hand. This particularly applies to waxy maize starch, which is commercially by far the most important waxy cereal starch. The cultivation of waxy maize, suitable for the production of waxy maize starch is not commercially feasible in countries having a cold or temperate climate, such as The Netherlands, Belgium, England, Germany, Poland, Sweden and Denmark. The climate in these countries, however, is suitable for the cultivation of potatoes. Tapioca starch, obtained from cassave, may be produced in countries having a warm climate, such as is found in regions of South East Asia and South America.

The composition and properties of root and tuber starch, such as amylopectin potato starch and amylopectin tapioca starch, differ from those of the waxy cereal starches. Amylopectin potato starch has a much lower content of lipids and proteins than the waxy cereal starches. Problems regarding odor and foaming, which, because of the lipids and/or proteins, may occur when using waxy cereal starch products (native and modified), do not occur, or occur to a much lesser degree when using corresponding amylopectin potato starch products. In contrast to the waxy cereal starches, amylopectin potato starch contains chemically bound phosphate groups. As a result, amylopectin potato starch

products in a dissolved state have a distinct polyelectrolyte character.

According to the invention, root and tuber starches are oxidized. Surprisingly, under the conditions of the present process, cereal and fruit starches are not degraded to a sufficient extent to obtain a product having the desired characteristics. The oxidation of amylopectin potato starch and amylopectin tapioca starch has been found to lead to particularly advantageous oxidized starches.

Suitable derivatives of the above specific starch to be used in an oxidation process according to the invention are obtainable by crosslinking, etherification, or esterification of the starch, or a combination of two or more of said modifications. These modifications may be performed in any known manner. Examples of suitable manners for obtaining the desired derivatives are for instance disclosed in "Modified Starches: Properties and Uses", O.B. Wurzburg, CRC Press Inc., 1987.

Within these classes of derivatives, particularly preferred derivatives to be oxidized are cationic, anionic and amphoteric starches. For the introduction of a cationic group, preferably a 2-hydroxypropyltrialkyl ammonium group is introduced on the starch. The alkyl chains of this quaternary ammonium compound may vary from 1 to 20 carbon atoms. For example, 1-chloro-2-hydroxypropyltrimethyl ammonium salt, glycidyltrimethyl ammonium salt, 1-chloro-2-hydroxypropyldimethylallyl ammonium salt or 1-chloro-2-hydroxypropylmethyldiallyl ammonium salt can be applied as cationization agent. Anionic substituents can be attached to the starch via an ether linkage. This may be achieved by reaction with for example chloroacetic acid of chloroacetic acid salts. Amphoteric derivatives may comprise any combination of the above cationic and anionic groups.

According to the invention, starch is oxidized using hydrogen peroxide. The amount of hydrogen peroxide employed is from about 0.01 to 5.0 wt.%, preferably about 0.05 to 2.5

wt.% anhydrous hydrogen peroxide on dry substance of the starch. The hydrogen peroxide will normally be used in the form of an aqueous solution, as commonly supplied in commerce.

Preferably, the oxidation reaction is performed in a solution, dispersion or suspension of the starch in water, to which the hydrogen peroxide, or an aqueous solution thereof, is added. Preferably, the hydrogen peroxide is added batchwise or dropwise.

Suitable concentrations of the starch in said solution, dispersion or suspension lie between 10 and 50, preferably between 20 and 40 wt.%, based on the weight of the solution, dispersion or suspension. The pH during the oxidation reaction will preferably around neutral and lie between pH 6.5 and 9.0. The temperature during the oxidation reaction in a suspension will preferably be below 60°C, more preferably between 20 and 50°C. When the reaction is carried out in a solution or dispersion, the temperature will usually be chosen between 60 and 200°C, preferably between 100 and 160°C. In order to carry out the reaction at a temperature higher than 100°C, use is preferably made of a jet cooker.

In accordance with the present invention, the oxidation of the specific starch described above is performed in the presence of a catalyst, which catalyst comprises divalent copper ions. The catalyst will preferably be used in the form of a salt. In principle, any copper(II)-salt which is soluble in water may be used. Suitably, the anion of the salt may be chosen from the group of chloride, sulfate, phosphate, nitrate, acetate, bromide and combinations thereof.

It is one of the great advantages of the present invention that the oxidation reaction proceeds very fast to a desired extent of degradation of the starch, while only very small amounts of the catalyst are used. More in particular, it has been found that such small amounts of catalyst suffice, that the amount of metal ions that ends up in the

process water (mother liquor) is acceptably low. Said process water can conveniently be disposed together with normal sludge disposal without encountering the risk that the microorganisms present in the sludge are exterminated.

Preferably, the quantity of copper used ranges from about 5 ppb to about 5000 ppb, more preferably from about 100 to about 1000 ppb, on dry substance of starch. When the oxidation reaction is carried out in a solution or a dispersion, the quantity of copper may be lower (e.g. between 5 and 1000 ppb) than when the reaction is performed in a suspension.

In a preferred embodiment, the action of the divalent copper ions is enhanced by calcium, vanadium, manganese, iron and/or tungsten ions. The counterions for these ions may be of the same type as those of the copper catalyst. These additional salts will preferably be used in an amount between about 100 and about 2000 ppm, on dry substance of starch.

The invention further relates to an oxidized starch obtainable by a process as described hereinabove, and to the use of said oxidized starch in the paper, adhesive, textile and food industries.

In the paper industry, oxidized starches have been used as coating binders since 1903. The main purpose of coating paper is to improve its printability. The most important components of a coating (also referred to as coating color) are pigments, such as titanium oxide, calcium carbonate, clays, and the like, binders, such as latices, starches, PVOH, proteins, and the like, and water. The present oxidized starches have been found to have excellent properties, such as a good viscosity stability when in solution or dispersion. This makes them highly suitable for use as a binder in paper coatings.

In another application, the present oxidized starch, particularly when prepared from a cationic starch derivative, may be used as an emulsifying agent for, or during production of, alkyl ketene dimers, alkyl succinic anhydride or alkyl

isocyanates (analogous to what has been described in e.g. WO-A-96/31650, EP-A-0 824 161 and EP-A-0 369 328).

In addition, it has been found that the present oxidized starch is highly suitable for replacing high viscous hydrocolloids, such as polyvinyl alcohol, guar, alginate, carboxymethylcellulose or hydroxyethylcellulose.

Yet another application wherein the present oxidized starch has been found to be highly suitable is in adhesives. The present oxidized starch may be used to adhere two or more layers of paper together to form a multi-layer paper or (card)board. Also, aluminum foil can suitably be adhered onto paper by use of an oxidized starch according to the invention. Further, the present oxidized starch may be used as a component in paper sack adhesives and wall paper adhesives, leading to an adhesive providing improved binding strength. In addition, paper and tape may be gummed with the present oxidized starch to produce stamps or envelopes. In abrasive paper or abrasive linen, the present oxidized starch may be used to adhere abrasive particles, such as sand, onto the paper or linen. In addition, the present oxidized starch may be used as an adhesive for seeds or fertilizers.

Still another application is related to the stabilization of emulsions, in particular of emulsions used in the adhesive industry such as polyvinylacetate emulsions. An oxidized starch according to the invention may be used as a protective colloid for providing the desired stability.

In the textile industry, the present oxidized starch may be used to improve the weaving operation or weaving efficiency by warp yarn sizing. This results in an improved abrasion resistance of the warp yarns during the weaving process and less warp-end breakages. The present oxidized starch may further be applied as finishing agent to give a smooth and firm hand to fabrics. It may also be used for the coating of glass fibers (fabrics and non-wovens). In addition, it may be used as blanket adhesive in the textile printing industry.

In the food industry, Arabic gum may be replaced in e.g. confectioneries by an oxidized starch according to the invention. Also, the present product has been found to be highly suitable as a thickener in various food products, such as sauces. The excellent stability of the present oxidized starch, leads in these applications to a more clear food product.

It will be clear to the skilled person that the above list of applications is not intended to be extensive and that many more applications of the present oxidized starches are conceivable. In practice, the present product may be used in any application in which oxidized starches have conventionally been used.

The invention will now be elucidated by the following non-restrictive examples.

EXAMPLES

Brookfield viscosity

The Brookfield viscosity (in mPa.s.) is measured at a 25 w/w% solution (dispersion) of the product in water at 50°C with a Brookfield viscometer (model RV-II+; 20 rpm). The stability of the starch solution was determined by measuring the Brookfield viscosity after 24 hours of storage at 50°C.

Intrinsic viscosity

The intrinsic viscosity, expressed in dL/g, is determined in a known manner, for instance as described in H.W. Leach in Cereal Chemistry, vol. 40, page 595 (1963), using an Ubbelohde viscosity meter and a 1 M sodium hydroxide in water as the solvent.

Peroxide test

The peroxide test is performed with Merckoquant 1.10081.0001 peroxide-test analytical test strips. The test was positive,

indicating that there was still some hydrogen peroxid in the reaction mixture, or negative, indicating that the hydrogen peroxide was consumed.

Example 1

2.5 mole of amylopectin potato starch was suspended in 633 g of demineralized water. The temperature of the suspension was increased to 40°C and 2.7 mL of a solution of 550 mg $CuSO_4.5H_2O$ in 1 L of demineralized water was added. 20 ml of a 30 wt.% hydrogen peroxide solution in water was added. During the oxidation the pH was maintained at 7.0 by the addition of a 4.4% sodium hydroxide solution in demineralized water. After 24 h of the reaction mixture the peroxide test was carried out. Subsequently, the mixture was neutralised to pH 5.0 by the addition of 10 N H_2SO_4, whereupon the product was dewatered and washed before drying.

Instead of amylopectin potato starch, potato starch, waxy corn starch or tapioca starch was used as starting material. Besides, 5.4 mL of a solution of 550 mg $CuSO_4.5H_2O$ in 1 L of demineralized water was added in stead of 2.7 mL. The results are shown in table 1.

Table 1 - The hydrogen peroxide oxidation of different starches at (8.0 g hydrogen peroxide per mole starch, 40°C, pH 7.0, during 24 hour) catalyzed by various amounts of copper-ions.

Starch-type (intrinsic viscosity starting material)	Cu ppb[3]	Peroxide test	Intrinsic viscosity (dL/g)	Brookfield viscosity (mPa.s.) after 0 and 24 hours storage at 50°C	
				0 h	24 h
Potato			2.54[2]		
	0	positive	2.52	n.a.[1]	
	932	positive	0.28	100.000	gel
	1858	negative	0.26	50.000	gel
Waxy-corn			1.69[2]		
	932	positive	1.66	n.a.[1]	
	1858	positive	1.50	n.a.[1]	
Tapioca			2.19[2]		
	932	positive	1.17	n.a.[1]	
	1858	positive	0.75	n.a.[1]	
Amylopectin potato			2.26[2]		
	0	positive	1.85	n.a.[1]	
	932	negative	0.20	37	37
	1858	negative	0.20	35	37

[1] n.a. = not available due to very high viscosity of the 25 w/w % suspension of the product

[2] Intrinsic viscosity of the starting material

[3] Amount of catalyst calculated on dry starch

Comparison of the results presented in table 1, shows that the hydrogen peroxide degradation of starch catalyzed by small amounts of copper ions is more efficient in the order: waxy corn starch < tapioca starch < potato starch <

amylopectin potato starch. Without the addition of copper ions the hydrogen peroxide of potato starch is negligible. Under the same reaction conditions amylopectin potato starch reacts slowly.

Besides, it can be seen that the viscosity of the solution of the degraded amylopectin potato starch during storage at 50°C is very stable. A solution of the degraded potato starch is very unstable and a gel is formed.

Example 2

The reaction of Example 1 was repeated with amylopectin potato starch and 0.0125 mole of calcium ions instead of $CuSO_4.5H_2O$.

The results are presented in table 2.

Example 3

The reaction of Example 1 was repeated with amylopectin potato starch and 0.0125 mole of calcium ions and 0.36 mL of a solution of 550 mg $CuSO_4.5H_2O$ in 1 L of demineralized water instead of 2.7 mL of a solution of 550 mg $CuSO_4.5H_2O$ in 1 L of demineralized water.

The results are presented in table 2.

Table 2 - The hydrogen peroxide oxidation of amylopectin potato starch at (8.0 g hydrogen peroxide per mole starch, 40°C, pH 7.0, during 24 hours) catalyzed by 1240 ppm calcium ions and a combination of 1240 ppm calcium ions and 110 ppb copper-ions.

Cu ppb[1]	Peroxid test	Brookfield viscosity (mPa.s.)	Intrinsic viscosity (dL/g)
0	positive	5150	1.38
110	positive	1620	1.10

[1] Amount of catalyst calculated on dry starch

The hydrogen peroxide oxidation of amylopectin potato starch is catalyzed by calcium ions. Calcium ions are less effective than copper ions. The combination of calcium ions and copper ions lead to a more effective degradation of the amylopectin potato starch.

Example 4

2.5 mole of cationic (MSin = 0.035) amylopectin potato starch was suspended in 633 g of demineralized water. The temperature of the suspension was increased to 40°C and 2.7 mL of a solution of 550 mg $CuSo_4.5H_2O$ in 1 L of demineralized water was added. 1.25 ml of a 30 wt.% hydrogen peroxide solution in water was added. During the oxidation the pH was maintained at 7.0 by the addition of a 4.4% sodium hydroxide solution in demineralized water. After 24 h of the reaction mixture the peroxide test was carried out. Subsequently, the mixture was neutralised to pH 5.0 by the addition of 10 N H_2SO_4, whereupon the product was dewatered and washed before drying.

Instead of cationic amylopectin potato starch, cationic potato starch (MSin = 0.035) was used as starting material. Besides, 2.5, 5.0 or 7.5 mL of a 30 wt.% hydrogen peroxide solution in water was added instead of 1.25 mL. The results are summarized in Table 3.

Table 3 - The hydrogen peroxide concentration of cationic potato starches (932 ppb Cu^{2+}, 40°C, pH 7,0 during 24 hours)

Starch type	30 wt.% H_2O_2 (mL/mol)	Peroxide test	Brookfield viscosity (mPa.s.) in 10 wt.% concentration
Cationic potato starch	0,50	positive	2300
	1,00	positive	290
	2,00	positive	66
	3,00	positive	28
Cationic amylopectin potato starch	0,50	negative	250
	1,00	negative	83
	2,00	negative	33
	3,00	negative	18

Example 5

2000 Grams of starch were suspended in 2L of water. To this suspension, 120 grams of a 25% solution of NaOH was added. The suspension was stirred for 30 minutes at 90°C. Subsequently, 75 grams of a 30% aqueous solution of hydrogen peroxide was added and the stirring was continued at the same temperature. The conditions employed are illustrative of a thermochemical conversion process.

The above procedure was performed twice. Once, the starch was regular potato starch (PS), and once the starch was amylopectin potato starch (APS). In the case of APS, the reaction was complete after 30 minutes, which was determined by establishing that no hydrogen peroxide was present. The obtained product was stable. In the case of PS, the reaction was complete after 60 minutes, which was determined by establishing that no hydrogen peroxide was present. The

obtained product was very unstable; even at 90°C a thickening effect was observed.

Claims

1. A process of oxidizing starch wherein a root or tuber starch comprising at least 95 wt.% based on dry substance of the starch of amylopectin, or a derivative thereof, is treated with hydrogen peroxide in the presence of a catalyst, which catalyst comprises divalent copper ions.

2. A process according to claim 1, wherein the catalyst is a copper(II)chloride, copper(II)sulfate, copper(II)phosphate, copper(II)nitrate salt, copper(II)acetate salt, copper(II)bromide salt or a combination thereof.

3. A process according to any one of the preceding claims, wherein the catalyst is present in an amount ranging from about 5 ppb to about 5000 ppb, preferably from 100 to about 1000 ppb, on dry substance of starch.

4. A process according to any one of the preceding claims, wherein the action of the divalent copper ions is enhanced by one or more of calcium, vanadium, manganese, iron or tungsten ions.

5. A process according to any of the preceding claims, wherein the starch is potato starch or tapioca starch.

6. A process according to any one of the preceding claims, wherein the hydrogen peroxide is used in an amount ranging from 0.01 to 5.0 wt.%, preferably from 0.05 to 2.5 wt.% on dry substance of starch.

7. A process according to any one of the preceding claims, wherein the derivative of the starch is a cationic, anionic or amphoteric starch.

8. An oxidized starch obtainable by a process according to any one of the preceding claims.

9. Use of an oxidized starch according to claim 8 as a binder in paper coatings or surface sizings, as an adhesive, in warp yarn sizing, as a coating of glass fibers, as a blanket adhesive, and in abrasive paper or in food products.

10. Use of an oxidized starch according to claim 8 as an emulsifying agent for an alkyl succinic anhydride, an alkyl ketene dimer or an alkyl isocyanate.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/NL 99/00568

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08B31/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 975 206 A (LOTZGESELL ET AL.) 17 August 1976 (1976-08-17) column 3, line 9 - line 29 claims; table 1	1-9
A	US 3 539 366 A (FOSTER G. EWING) 10 November 1970 (1970-11-10) column 2, line 40 - line 46 claims	1-3,5,6, 8,9

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 December 1999	09/12/1999

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 99/00568

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	P. PAROVUORI ET AL.: "Oxidation of potato starch by hydrogen peroxide" STÄRKE, vol. 47, no. 1, 1995, pages 19-23, XP002091292 de page 19, left-hand column, line 29 - line 36 page 20, line 11 - line 32 page 21, right-hand column, line 9 - line 19 ---	1-6,8
A	R. L. WHISTLER ET AL.: "Oxidation of amylopectin with hydrogen peroxide at different hydrogen ion concentrations" THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 81, 1959, pages 3136-3139, XP002091293 usa page 3138, left-hand column, line 47 -right-hand column, line 27 ---	1
A	CHEMICAL ABSTRACTS, vol. 123, no. 12, 18 September 1995 (1995-09-18) Columbus, Ohio, US; abstract no. 147114, "Substitued succinic anhydride-containing sizing emulsions for surface sizing of newsprint paper" XP002091294 abstract & JP 07 138898 A (ARAKAWA CHEM IND) 30 May 1995 (1995-05-30) ---	10
A	US 3 655 644 A (H. W. DURAND) 11 April 1972 (1972-04-11) cited in the application -----	

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter: nal Application No
PCT/NL 99/00568

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3975206 A	17-08-1976	NONE	
US 3539366 A	10-11-1970	NONE	
JP 07138898 A	30-05-1995	NONE	
US 3655644 A	11-04-1972	NONE	